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PL 4105 Provisional

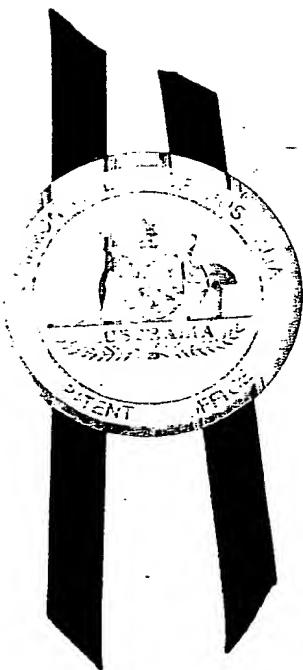
I, NICHOLAS IAN MCCONCHIE, ACTING ASSISTANT DIRECTOR PATENT ADMINISTRATION, hereby certify that the annexed is a true copy of the Provisional specification as filed on 14 August 1992 in connection with Application No. PL 4105 for a patent by TECHNOLOGICAL RESOURCES PTY LTD filed on 14 August 1992.

I further certify that the annexed specification is not, as yet, open to public inspection.

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WITNESS my hand this Nineteenth day of August 1993.

Nicholas Ian McConchie
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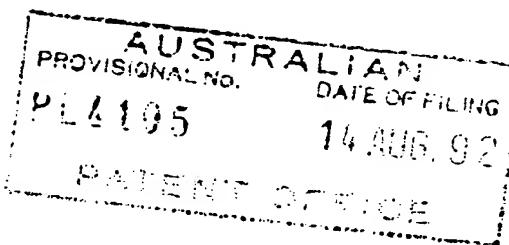
PROVISIONAL SPECIFICATION

Applicant:

TECHNOLOGICAL RESOURCES PTY LTD
A.C.N. 002 183 557

Invention Title:

UPGRADING TITANIFEROUS MATERIALS



The invention is described in the following statement:

UPGRADING TITANIFEROUS MATERIALS

This invention relates to the removal of impurities from naturally occurring and synthetic titaniferous materials for the purpose of enhancing the behaviour of the materials in industrial chlorination systems, as used in the production of titanium metal and titanium dioxide pigments.

Embodiments of the present invention have the common feature of roasting of titaniferous materials in the presence of additives and at temperatures which encourage the formation of a siliceous liquid phase, followed at some stage by cooling and aqueous leaching as steps in an integrated process. Additional steps may be employed as will be described below.

In industrial chlorination processes titanium dioxide bearing feedstocks are fed with coke to chlorinators of various designs (fluidised bed, shaft, molten salt), operated to a maximum temperature in the range 700 - 20 1200°C. The most common type of industrial chlorinator is of the fluidised bed design. Gaseous chlorine is passed through the titania and carbon bearing charge, converting titanium dioxide to titanium tetrachloride gas, which is then removed in the exit gas stream and condensed to liquid 25 titanium tetrachloride for further purification and processing.

The chlorination process as conducted in industrial chlorinators is well suited to the conversion of pure titanium dioxide feedstocks to titanium tetrachloride. 30 However, most other inputs (ie. impurities in feedstocks) cause difficulties which greatly complicate either the chlorination process itself or the subsequent stages of condensation and purification. The attached table provides an indication of the types of problems

encountered. In addition, each unit of inputs which does not enter products contributes substantially to the generation of wastes for treatment and disposal. Some inputs (eg. heavy metals, radioactives) result in waste classifications which may require specialist disposal in monitored repositories.

Preferred inputs to chlorination are therefore high grade materials, with the mineral rutile (at 95-96% TiO₂) the most suitable of present feeds. Shortages of rutile have led to the development of other feedstocks formed by upgrading naturally occurring ilmenite (at 40-60% TiO₂), such as titaniferous slag (approximately 86% TiO₂) and synthetic rutile (variously 92-95% TiO₂). These upgrading processes have had iron removal as a primary focus, but have extended to removal of manganese and alkali earth impurities, as well as some aluminium.

	Elemental Input	Chlorination	Condensation	Purification
20	Fe, Mn	Consumes chlorine, coke, increases gas volumes	Solid/liquid chlorides foul ductwork, make sludges	
25	Alkali & alkali earth metals	Defluidise fluid beds due to liquid chlorides, consume chlorine, coke		
30	Al	Consumes chlorine, coke	Causes corrosion	Causes corrosion makes sludges
35	Si	Accumulates in chlorinator, reducing campaign lime. Consumes coke, chlorine	Can encourage duct blockage. Condenses in part with titanium tetrachloride	May require distillation from product
40				
45				

V

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Must be
removed, by
chemical
treatment and
distillation

10

Th Accumulates
 in
 chlorinator
 brickwork,
 radioactive;
 causes
 disposal
 difficulties

15

In the prior art synthetic rutile has been formed from titaniferous minerals, eg. ilmenite, via various techniques. According to the most commonly applied technique, as variously operated in Western Australia, the titaniferous mineral is reduced with coal or char in a rotary kiln, at temperatures in excess of 1100°C. In this process the iron content of the mineral is substantially metallised. Sulphur additions are also made to convert manganese impurities partially to sulphides. Following reduction the metallised product is cooled, separated from associated char, and then subjected to aqueous aeration for removal of virtually all contained metallic iron as a separable fine iron oxide. The titaniferous product of separation is treated with 2-5% aqueous sulphuric acid for dissolution of manganese and some residual iron. There is no substantial chemical removal of alkali or alkaline earths, aluminium, silicon, vanadium or radionuclides in this process as disclosed or operated. Further, iron and manganese removal is incomplete.

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Recent disclosures have provided a process which operates reduction at lower temperatures and provides for hydrochloric acid leaching after the aqueous aeration and iron oxide separation steps. According to these disclosures the process is effective in removing iron, manganese, alkali and alkaline earth impurities, a

substantial proportion of aluminium inputs and some vanadium as well as thorium. The process may be operated as a retrofit on existing kiln based installations. However, the process is ineffective in full vanadium removal and has little chemical impact on silicon.

In another prior art invention relatively high degrees of removal of magnesium, manganese, iron and aluminium have been achieved. In one such process ilmenite is first thermally reduced to substantially complete reduction of its ferric oxide content (ie. without substantial metallisation), normally in a rotary kiln. The cooled, reduced product is then leached under 35 psi pressure at 140-150°C with excess 20% hydrochloric acid for removal of iron, magnesium, aluminium and manganese. The leach liquors are spray roasted for regeneration of hydrogen chloride, which is recirculated to the leaching step.

In other processes the ilmenite undergoes grain refinement by thermal oxidation followed by thermal reduction (either in a fluidised bed or a rotary kiln). The cooled, reduced product is then subjected to atmospheric leaching with excess 20% hydrochloric acid, for removal of the deleterious impurities. Acid regeneration is also performed by spray roasting in this process.

In all of the above mentioned hydrochloric acid leaching based processes impurity removal is similar. Vanadium, aluminium and silicon removal is not fully effective.

In yet another process ilmenite is thermally reduced (without metallisation) with carbon in a rotary kiln, followed by cooling in a non-oxidising atmosphere. The cooled, reduced product is leached under 20-30 psi gauge pressure at 130°C with 10-60% (typically 18-25%) sulphuric acid, in the presence of a seed material which assists

hydrolysis of dissolved titania, and consequently assists leaching of impurities. Hydrochloric acid usage in place of sulphuric acid has been claimed for this process. Under such circumstances similar impurity removal to that
5 achieved with other hydrochloric acid based systems is to be expected. Where sulphuric acid is used radioactivity removal will not be complete.

A commonly adopted method for upgrading of ilmenite to higher grade products is to smelt ilmenite with coke
10 addition in an electric furnace, producing a molten titaniferous slag (for casting and crushing) and a pig iron product. Of the problem impurities only iron is removed in this manner, and then only incompletely as a result of compositional limitations of the process.

15 A wide range of potential feedstocks is available for upgrading to high titania content materials suited to chlorination. Examples of primary titania sources which cannot be satisfactorily upgraded by prior art processes for the purposes of production of a material suited to
20 chlorination include hard rock (non detrital) ilmenites, siliceous leucoxenes, many primary (unweathered) ilmenites and large anatase resources. Many such secondary sources (eg. titania bearing slags) also exist.

Clearly there is a considerable incentive to discover
25 methods for upgrading of titaniferous materials which can economically produce high grade products almost irrespectively of the nature of the impurities in the feed.

Accordingly the present invention provides processing steps which may be incorporated into more general processes
30 for the upgrading of titaniferous materials, rendering such processes applicable to the treatment of a wider range of feeds and producing higher quality products than would otherwise be achievable.

The processing steps of interest are:

(i) mixing of titaniferous materials with additives which encourage the formation of a siliceous liquid phase and titaniferous solid phases upon subsequent heating to temperatures below 1300°C. (This process step will generally be necessary but might not be important for some materials which can spontaneously produce siliceous liquid phases upon heating).

(ii) heating of the mixture resulting from step (i) to temperatures sufficient to produce a siliceous liquid phase and a solid titaniferous phase, followed by cooling at a sufficient rate to ensure susceptibility of the solidified material to the removal of silica in step (iii).

(iii) leaching of the product of step (ii) in a leaching step in which the effective leach reagent is either an alkali metal hydroxide or water, depending on the composition of the liquid phase of step (ii), conducted in such a manner as to remove at least a portion of the contained silicon.

It has been discovered that the above processing steps have the effects of allowing effective removal of silica, and phosphorus, partial removal of alumina, and complete removal of vanadium. In concert with other processing steps (particularly involving hydrochloric acid) it is possible to obtain almost complete removal of iron, silicon, aluminium, phosphorus, magnesium and other alkaline earths, alkalis, rare earths, thorium and radioactivity, which impurities form an almost comprehensive list of impurities in titaniferous mineral sources. From most materials a product purity of greater than 97% TiO_2 can be obtained.

The mixing step may range from direct mixing of additives prior to charging to thermal treatment to more complex feed preparations such as the formation of agglomerates or nodules of mixed products, to briquette production from feeds and additives.

Thermal processing may be carried out in any suitable device. The production of liquid phases would recommend rotary or grate kilning, but shaft furnaces may also be used. Any gaseous atmosphere conditions may be used, from fully oxidising to strongly reducing. Thermal processing atmosphere should be chosen to most suit other steps in integrated processing. Reducing conditions may be achieved where desired by either the use of a sub stoichiometric firing flame or the addition of coal, char or coke with the thermal processing charge.

Thermal processing residence time at temperature will depend on the nature of the additives and the feed, as well as the operating temperature. Residence times of from 30 minutes to five hours have been effective, allowing thermal processing residence times to be set to most suit other requirements in integrated processing.

Cooling of the thermally treated material should be conducted in such a manner as to limit the reversion of silicates to silica and titanates, ie. should be at a rate sufficient to reach a temperature at which the liquid silicate phase solidifies as to ensure the formation of a solid glass rather than complete formation of crystalline products. Further, cooling should be conducted under an environment appropriate to the conditions of thermal treatment (ie. reduction processing will require cooling in an oxygen free environment).

The aqueous leaching step need not necessarily follow directly after the presently disclosed thermal processing step. For example if the thermal processing step is

conducted under oxidising conditions it may be optionally followed by a reduction step prior to aqueous leaching. Further crushing/grinding of the thermally processed material to enhance subsequent leach performance may be
5 undertaken.

The conditions necessary to conduct effective leaching will depend on the nature of the original feed and the additives. For example, addition of soda ash to siliceous leucoxene in accordance with the present disclosure will result in a product which can be leached in sodium silicate solution formed directly from the thermally treated material; the active leachant in this case is simply water. In other cases up to 100 gPL caustic soda solution will be an effective leachant. Leaching will
10 generally benefit substantially by use of high temperature (eg. 100°C or above), although it has not been necessary to use pressure leaching to achieve effective conditions.
15 Nevertheless it is presently disclosed that pressure leaching can be effectively and successfully applied.
20 Lower temperatures can also be used, although with penalties in process kinetics.

Leaching may be conducted in any circuit configuration, including batch single or multiple stage leaching, continuous concurrent multistage leaching, or
25 continuous countercurrent multistage leaching. For most circumstances two stage concurrent leaching will be most beneficial. Average residence time may vary from 30 minutes to 10 hours, depending on process conditions. Any leach vessel capable of providing adequate shear may be
30 used. Simple stirred tank vessels are applicable.

At the conclusion of leaching the leach liquor may be separated from the mineral by any suitable means, including thickening, filtration and washing. The mineral product may then pass on to other steps in an integrated process.

For example, an acid leach may follow the disclosed leaching step, particularly where the titaniferous feed has a content of alkalis or alkaline earths.

An example of an embodiment of the disclosed processing steps into an integrated mineral upgrading process follows. Titaniferous mineral containing iron, silicon, magnesium, manganese, vanadium and aluminium is wet milled to a passing size of 100 microns and dewatered by belt filtration to 5% moisture. The dewatered mineral is fed to a high intensity mixer into which is sprayed a hot solution of sodium carbonate (eg. at 25 wt%). The moist mixture is then fed to a rotary dryer wherein nodules of dried material (eg. passing 1mm) are formed. The dried material is mixed with a small amount of coal and recycled char and fed to a rotary kiln in which it is heated to a maximum temperature of 1000°C for residence times which avoid substantial metallisation, and then cooled in a sealed rotary cooler. The cooled material is separated from char by sizing and magnetic separation. The separated treated mineral is then leached at 100°C in a solution of sodium silicate which is itself the product of the leach. After filtration and washing the leached material is then leached with hydrochloric acid (eg. at an acid strength of 5-10% HCl at 100°C), after which the material is washed and filtered again.

After such processing (optimised for a particular material) it is to be expected that removal of 98% of the contained iron, 90% of contained magnesium and manganese, 95% of contained silicon, phosphorus and vanadium and 85% of contained aluminium will have been achieved. Further, 80% of contained thorium will also have been removed. The dried product will normally contain greater than 97% TiO₂.

The above example is only one of a number of possible schemes for incorporating the disclosed processing steps

into integrated processes for the upgrading of general titaniferous materials to high grade products.

5 DATED THIS 14 DAY OF AUGUST 1992

TECHNOLOGICAL RESOURCES PTY LIMITED

By its Patent Attorneys:

GRIFFITH HACK & CO

10 Fellows Institute of Patent
Attorneys of Australia

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